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Treatment Technologies for Hazardous Wastes Part 4. A Review of Alternative Treatment Processes for Metal Bearing Hazardous Waste Streams

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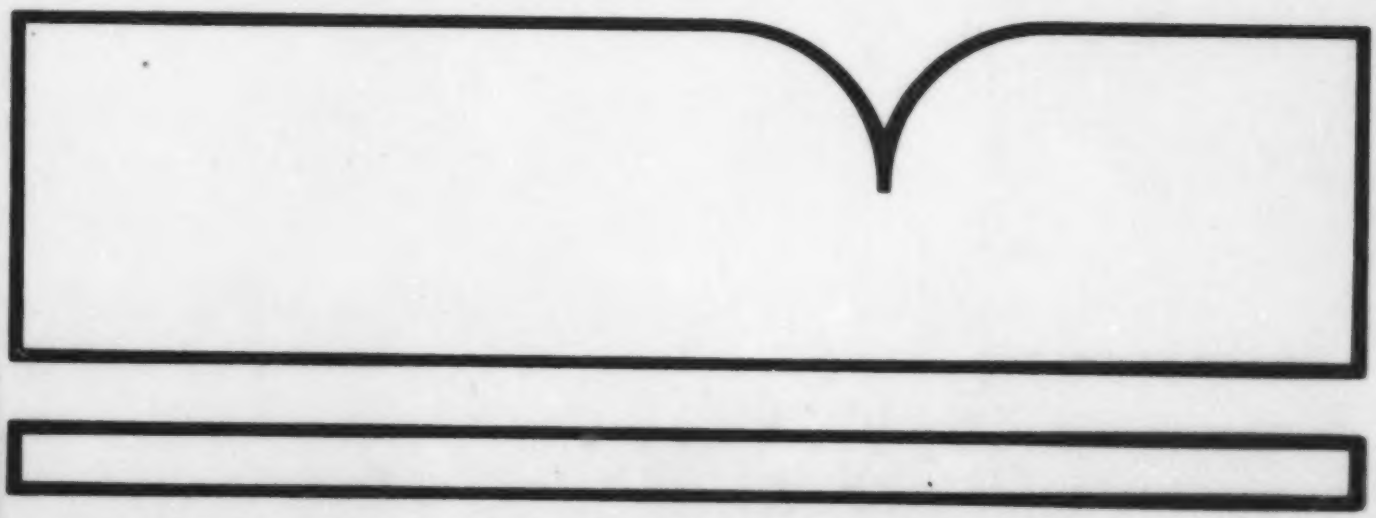

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16. ABSTRACT

The United States Congress and the U.S. Environmental Protection Agency (EPA) believe that treatment and recovery techniques should be given maximum priority when considering methods for managing the Nation's generated hazardous waste. A prohibition for the disposal of certain categories of hazardous wastes either directly onto or into the land without being treated to an accepted degree prior to such disposal practice has been promulgated. Wastes containing toxic metals and cyanide complexes have been selected as a group to be restricted. Due to the high generation rate associated with this category, a large capacity of waste treatment processing will be required. Existing and emerging treatment alternatives which are or have the potential to be employed for waste treatment of metal bearing wastes are presented in this paper.

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HAZARDOUS WASTE MANAGEMENT

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TREATMENT TECHNOLOGIES FOR HAZARDOUS WASTES: PART IV

A Review of Alternative Treatment Processes for

Metal Bearing Hazardous Waste Streams

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The U.S. Congress and the U.S. Environmental Protection Agency believe that treatment and recovery techniques should be given maximum priority when considering methods for managing the nation's generated hazardous waste. A prohibition for the disposal of certain categories of hazardous wastes either directly onto or into the land without being treated to an accepted degree prior to such disposal practice has been promulgated.[1] Wastes containing toxic metals and cyanide complexes have been selected as a group to be restricted. Due to the high generation rate associated with this category, a large capacity of waste treatment processing will be required. Existing and emerging treatment alternatives which are or have the potential to be employed for waste treatment of metal bearing wastes are presented in this paper.

An estimated 7.9 billion gallons of metal bearing wastes, 4.7 billion gallons of cyanide wastes and 0.8 billion gallons of reactive wastes containing cyanides were generated in the United States in 1983.[2] Currently, 85 percent of all metal and cyanide bearing wastes that are subjected to land disposal are aqueous (≤ 1 percent total solids). A listing of the principal number of waste generators are listed by SIC code in Table I.[2]

The purpose of this review is to describe current treatment practices that are being used or considered for use at on-site or commercial hazardous waste treatment, storage and disposal facilities (TSDF) to treat metal and cyanide wastes conventionally land disposed.

Waste Characterization

Hazardous wastes which can be categorized as metal and cyanide bearing wastes are included in each of the five source designations for hazardous wastes as designated by EPA (40 CFR). The source categories are:

- D Wastes which are hazardous because they exhibit a particular hazardous characteristic, such as toxicity;
- F Wastes from non-specific sources;
- K Wastes from specific sources;
- P Acutely hazardous constituents; and
- U Toxic constituents

As is illustrated by Table II, the majority of metal/cyanide wastes generated in this country are characteristic toxic metal wastes (D) and wastes that result from electroplating and metal treating processes (F). These wastes are specified by the following RCRA codes:

- D002 Corrosive metal wastes which are aqueous and have a pH less than or equal to 2 or greater than or equal to 12.5.
- D003 A solid waste that exhibits the characteristics of reactivity in the presence of the cyanide ion, but is not listed as a hazardous waste in Part 2613.
- D004 Arsenic
- D005 Barium
- D006 Cadmium
- D007 Chromium
- D008 Lead
- D009 Mercury
- D010 Selenium
- D011 Silver
- F006 Wastewater treatment sludges from electroplating operations except from the following processes: 1) sulfuric acid anodizing of aluminum; 2) tin plating on carbon steel; 3) zinc plating (segregated basis) on carbon steel; 4) aluminum or zinc-aluminum plating on carbon steel; 5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and 6) chemical etching and milling of aluminum.
- F007 Spent cyanide plating bath solutions from electroplating operations (except for precious metals electroplating spent cyanide plating bath solutions).
- F008 Plating bath sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process (except for precious metals electroplating plating bath sludges).
- F009 Spent stripping and cleaning bath solutions from electro-

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Table I. Number of waste generators by SIC code.

No. of facilities (Dun's 1983)	SIC description	Weighted No. of facilities SIC	CN	Metals	Metals +CN
4,287	Plating and polishing	3471	750	263	1013
2,145	Paints and allied products	2851	20	212	232
2,902	Metal coating and allied products	3479	46	149	195
4,151	Motor vehicle parts and accessories	3714	62	107	169
2,183	Industrial inorganic chemicals	2819	3	131	134
876	Metals, nonferrous, secondary	3341	37	93	130
55,380	Fabricated metal products	3400	51	73	124
393	National security	9711	16	84	100
966	Motors and generators	3721	40	61	100
32,867	Misc. manufacturing industries	3900	23	68	91
384	Metal, nonferrous, rolling, drawing	3356	30	60	90
609	Printing ink	2893	0	89	89
1,229	Blast furnaces, steel mills	3312	11	78	89
1,229	Foundries, gray iron	3321	0	82	82
2,614	Electric services	4911	0	81	81
1,160	Industrial organic chemicals	2869	5	80	85
1,529	Plastics material	2821	7	76	83
4,656	Radio and TV communication equipment	3662	30	49	79
5,392	Electronic components	3679	35	42	77
1,040	Motor vehicle bodies	3711	41	34	75
3,432	Machine tool accessories	3545	40	0	40

plating operations where cyanides are used in the process (except for precious metals electroplating bath sludges).

F010 Quenching bath sludge from oil baths from metal heat treating operations where cyanides are used in the process (except for precious metals heat treating quenching bath sludges).

F011 Spent cyanide solutions from salt bath pot cleaning from metal heat treating operations (except for precious metals heat treating spent cyanide solutions from salt bath pot cleaning).

F012 Quenching wastewater treatment sludges from metal heat treating operations where cyanides are used in the process (except for precious metals heat treating quenching wastewater treatment sludges).

Other hazardous wastes containing metals and/or cyanide constituents are generated from specific industrial sources (RCRA Code K), such as inorganic chemicals and pigments (K002–8), petroleum refining (K052), iron and steel (K061, K062), secondary lead (K069, K100), and ink formulations (K086). Salts of the various metal ions and cyanide complexes are listed in Part 261.33 (e) and (f) as discrete chemical constituents of discarded commercial chemical products, off-specification species, container residues and spill residues of acutely hazardous (P) and toxic (U) wastes respectively. Metal ions are prevalent in many forms based upon the type of industrial processes and uses employed.

Alternative Treatment Technologies for Metal Bearing Wastes

The U.S. EPA is interested in defining available technologies for each of the relevant hazardous waste codes. Technologies to be considered as alternatives to land disposal practices must demonstrate an acceptable level of treatment before these processes are permitted for operation. Treatment standards for many waste codes are being established through case studies, demonstration projects and pilot studies. A review of some of the existing alternative treatment options for metal/cyanide bearing wastes will be presented.

Discussions of how various treatment processes can achieve acceptable treatment objectives can be generalized by the approach presented in Figure 1. Although this simplification and reduction of waste treatment options does not account for all metal bearing wastes, a majority of these wastes will incorporate some aspect of the presented waste treatment strategy.

Due to the wealth of information found in the literature describing pretreatment practices associated with specific waste discharges, the following discussion is limited to two basic waste management approaches:

- Waste treatment processes
- Waste reduction and recovery

Processes are listed and synopsized for each main category with a description of their capabilities, advantages, limitations, significant results and relevance to standards and regulations. Discussion of a particular technology should not be construed as an endorsement by EPA. Likewise, absence of discussion for a particular technology does not imply a lack of confidence by

Table II. Generated waste distribution.

Hazardous waste group	Metals Annual volume (million gals.)	Metals Percent of total metals	Metals No. of generators	Cyanides Annual volume (million gals.)	Cyanides Percent of all CN	Cyanides No. of generators
D wastes	3,685	46.9	3,860	Est. 750	—	Not available
F wastes	3,920	49.9	2,091	3,920	83	2,091
K wastes	219	2.8	402	572	12.1	10
P wastes	28.3	.36	405	226	4.8	800
U wastes	5.2	.07	365	3.92	.08	306
Total	7,858		6,586	4,723		2,781

EPA in treating a particular waste stream. Rather, in the judgement of the author, the processes listed are to have potential for use to treat the subject waste. Regulatory and permitting requirements for installation and operation of the technologies presented may vary among local, state and federal authorities.

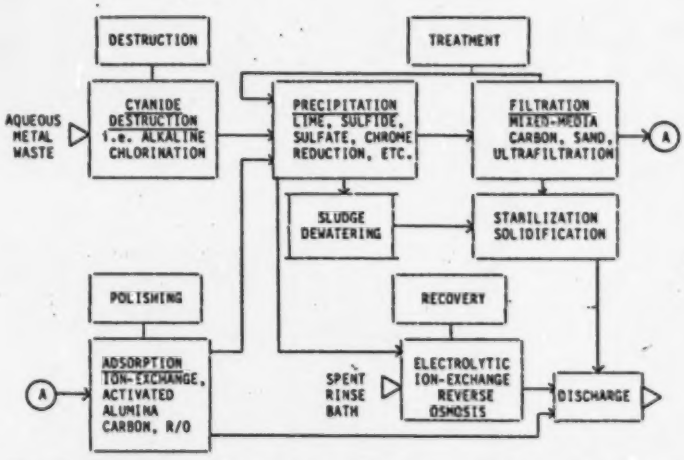


Figure 1. A general treatment approach for aqueous metal/cyanide bearing waste streams.

Waste Treatment Processes

Traditional approaches used to treat aqueous metal bearing wastes, other than land disposal, include:

- Precipitation: alkali, sulfide magnesium oxide
- Reduction: chromate, selenites, selenates and osmium tetroxide
- Stabilization/solidification
- Cyanide destruction
- Biological treatment

Table III shows treatment practices currently employed to treat representative metal bearing hazardous wstes for each major hazardous source category.[2] Cyanide treatment processes will be discussed separately in a later section.

Precipitation

Precipitation is the most preferred treatment process employed to remove toxic heavy metals from electroplating wastewaters. This method is used by approximately 75 percent of the electroplating facilities treating aqueous metal bearing wastes. The bulk of electroplating wastewater treatment sludges are usually in the form of metal hydroxides.[4] Precipitation techniques currently being practiced on spent process waters include hydroxide, lime and/or sulfide treatment.

(*1*) *Lime Precipitation.* Lime precipitation is a well-established process, perhaps the most commonly used process for treatment of aqueous metal bearing wastes. Lime (in slurry or solution) or caustic soda is added to the waste as a source of hydroxide ion raising the pH to a suitable level for optimum precipitation of the metal hydroxides.[5]

The metal hydroxide precipitate forms a floc which is afterwards removed from the water by gravity settling or filtration. Effluents and residual wastewaters containing excess hydroxide may require neutralization before discharge. Sludges precipitated from treatment may require fixation or encapsulation to ensure post disposal non-leachability. Because the optimum pH for hydroxide precipitation is different for each metal ion, treatment of mixed-metal aqueous wastes may require some adjustment. However, this adjustment must stay within the limits of regulation. Typically, hydroxide precipitation is optimum at a pH between 9.5 and 12.[6] Some of the hazardous wastes currently being treated by lime precipitation include corrosives (D002), metal finishing wastewaters and sludges (F006-12) after cyanide destruction, spent pickle liquor from steel finishing operations (K062) and leachates from scondary lead smelting (K100).[7]

Disadvantages encountered when employing lime precipitation are: limitation of metals removal due to solubility constraints of the metal hydroxides for variable wastewater matrices; interferences associated with complexing agents, e.g., cyanide, ethylenediaminetetraacetic acid (EDTA) etc., and difficulty encountered when stabilizing metal hydroxide sludges.

(*2*) *Magnesium Oxide Precipitation.* One precipitation agent which has shown promise for removal of heavy metal ions is magnesium oxide. To improve technology for treating process waters Schiller *et al.*, of the U.S. Bureau of Mines have shown in a research study that magnesium oxide (MgO) has many advantages over lime or caustic soda for precipitating metal hydroxides.[8] Due to the MgO's propensity for insolubility, lower sludge volumes are produced as the hydroxide sludge becomes more compact. The MgO-metal hydroxide sludge also cements together upon standing, thus hindering resuspension of the metal ions. One factor contributing to this phenomenon is the positive surface charge on MgO complementing the negative surface charge on most heavy metal hydroxides. Hence, water is expelled from the spaces between the particles yielding a more condensed solid. Also, MgO-hydroxide sludge is more easily dewatered.

Although the cost of MgO is greater than the cost of lime, for aqueous wastes with lower dissolved metals concentrations, the savings in sludge handling may outweigh the precipitant costs. Results from treating a spent process water sample comparing final metal concentrations after MgO and lime addition are presented in Table IV.[8]

From three- to fourfold stoichiometric excess of MgO is required to reach adequate pH values which range from 8 to 9. Lower residual metals concentrations can be observed for both settled and filtered MgO addition as compared to lime addition.

(*3*) *Sulfide Precipitation.* Sulfide precipitation is a process that produces

Table III. Alternative treatment processes for representative metal bearing wastes.[a]

Hazardous waste		Waste treatment class				
		Precipitation		Reduction		
Source	Code	Sulfide	Lime	Cr^b	Selenite, selenate	Stabilization/ solidification
1. EP toxic (D)	D002	X	X	X		
	D004					X
	D005		X			X
	D006	X	X			X
	D007		X	X		X
	D008	X				X
	D009	X				X
	D010				X	
	D011	X				X
2. Nonspecific (F)	F006	X	X	X		X
	F007	X				X
	F008	X				X
	F009					
	F019			X		X
3. Specific industrial (K)	K002-6			X		X
	K008		X	X		X
	K021	X				X
	K044	X				X
	K046	X				X
	K059	X				X
	K061		X			X
	K062		X			X
	K071	X		X		X
	K086			X		X
	K100	X				X
	K106	X				X
4. Toxic (U) and acutely hazardous (P) constituents, salts of:	P013		X			X
	P087				X	
	U032			X		X
	U204				X	
mercury		X				X
lead		X				X
thallium		X				X
arsenic		X				X
cadmium		X				X
silver		X				X
antimony		X				X
vanadium		X				X

[a] This table does not include cyanide treatment processes which will be presented in a later section.
[b] Insoluble chromates with low solubilities require longer reaction times followed by subsequent treatment.

the precipitation of a metal ion as a metal sulfide (MS) through contact between a metal ion (M^{+2}) and a sulfide ion (S^{-2}):

$$M^{+2} + S^{-2} \rightarrow MS \qquad (1)$$

Most heavy metals associated with electroplating wastes will form relatively stable metal ions. Exceptions to this rule include the trivalent chromic and ferric ions. The two processes currently employed to precipitate metals as sulfides are soluble sulfide precipitation (SSP) and insoluble sulfide precipitation (ISP).

SSP processes use water-soluble sulfide compounds, such as NaHS, which yield relatively higher concentrations of dissolved sulfide than the ISP process. As a result rapid precipitation of dissolved metals occurs. This rapid precipitation reaction induces discrete particle settling rather than nucleation precipitation of a particle from solution onto an existing substrate. SSP precipitation tends to result in a poor settling or filtering floc. However, this tendency can be reversed when additional coagulant and/or flocculant aids are used to enhance settling. Another disadvantage of the SSP process is that under certain pH conditions (pH <9), H_2S can evolve from dissolved sulfide ions. The rate of H_2S formation in a water solution is a direct function of pH and sulfide ion concentration. The H_2S creates an odor problem which can be mitigated by enclosing and venting process vessels.

The ISP process mixes the wastewater with a slurry of slightly soluble FeS which dissociates to satisfy its solubility product. This has the effect of controlling the level of dissolved sulfide at concentrations low enough to eliminate any detectable emission of H_2S. One advantage of the ISP process is the ability of combined sulfide and ferrous ions to reduce hexavalent chromium to its trivalent state. This eliminates the need to segregate and treat chromium wastes separately. A generalized treatment scheme for the ISP process is illustrated by Figure 2.[9]

There are numerous examples where specific applications of sulfide precipitation have been used to treat aqueous metal bearing hazardous wastes. One commercial facility used a two-stage precipitation process in which initial pH adjustment to 11 was followed by alum addition to pH 9.5 and final dosing with sodium bisulfite. Influent wastewaters (without chelating agents) contained up to 300 ppm Cd, 15,000 ppm Cr, 10,000 ppm Cu, 120,000 ppm Fe, 10,000 ppm Pb and 10,000 ppm Ni. After flocculation and clarification, the effluent met NPDES requirements for discharge to the municipal sewer.[6]

In another demonstration, the U.S. Army Belvoir R&D Center constructed and operated an SSP treatment system which was designed by JRB Associates. This SSP treatment system achieved a level of treatment comparable to that of lime precipitation coupled with filtration. Performance data are summarized in Table V.[10]

Sulfide precipitation of heavy metals

Table IV. Results from treating sample process water with MgO and lime.

Sample process water	Chemical analysis, ppm								
	pH	Fe	Cu	Zn	Ni	Mn	Co	Cd	Pd
Pretreatment	4.2	ND	8.7	ND	12.0	ND	11.1	ND	ND
0.4 g/l MgO, filtered	8.9	ND	<0.1	ND	<0.2	ND	<0.2	ND	ND
0.4 g/l MgO, filtered	8.9	ND	0.5	ND	0.2	ND	0.2	ND	ND
0.1 g/l lime, settled	9.4	ND	0.7	ND	1.2	ND	1.6	ND	ND

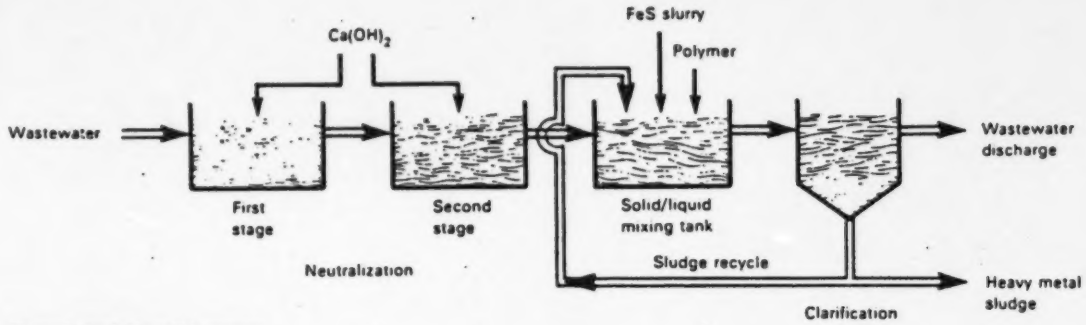


Figure 2. Insoluble sulfide process.

can be influenced adversely by chelating agents, such as EDTA, citrate, etc., however not as much as with hydroxide precipitation.[11] Advantages of sulfide precipitation include attainment of a high degree of metal removal; low detention time requirements in the reactor due to the high reactivities of sulfide; selective metal recovery; better sludge thickening and less leachability at pH 5 compared with the hydroxide sludge.[12]

Table V. Soluble sulfide treatment system performance.

Compound	Average concentration Influent (mg/L)	Effluent (mg/L)	Metals limits (30 day average) (mg/L)
Cd	2.06	0.10	0.26
Cr	2.61	0.32	1.71
Cu	1.82	0.04	2.07
Pb	1.04	0.19	0.43
Ni	3.50	0.07	2.38
Zn	5.8	0.41	1.48

Reduction

Chemical reduction has gained acceptance in industry for reducing complexed metals, such as nickel, copper, hexavalent chromium waste, soluble lead, silver, metal-containing cyanide and mercury. Chemical reduction is most effective when the aqueous metal wastes are relatively devoid of organic compounds. Chromium is usually reduced by sodium sulfite salts, sulfur dioxide and sulfuric acid. Iron, aluminum and zinc have shown potential for reducing chromium wastes. Sodium borohydride ($NaBH_4$) has recently shown promise for reducing and removing soluble lead, including organo-lead salts, from tetra-alkyl lead manufacturing wastes.[6]

(*1*) *Chromium Reduction.* Hexavalent chromium may be reduced from a valence state of (+6) to the less toxic trivalent chromium salts (+3). Some of the RCRA wastes which have been treated by chromate reduction are listed in Table VI.[2]

Several aqueous based processes which are commercially practiced are listed below:[2]

1. *Hydrosulfide reduction.* A sulfide ion is added to the chromate waste with pH adjustment to 7. After allowing a few hours for reaction the pH is adjusted to the alkaline side where chromic hydroxide is precipitated and filtered.
2. *Sulfur dioxide reduction.* Gaseous sulfur dioxide is added under pressure to the chromate containing solution, whereby the pH is lowered to an acidic level. Chromic hydroxide is precipitated after alkali addition and filtered.
3. *Ferrous ion precipitation.* Waste pickle liquor is frequently used to initiate a rapid reaction with ferrous ions under acidic conditions. Chromic hydroxide is formed with iron hydroxides and is precipitated under alkaline conditions. The resultant precipitate is filtered for removal.

Wastewaters generated by the above three treatment processes will require secondary treatment to remove sulfides and/or sulfites.

Chemical reduction is very efficient, with ≥ 90 percent reduction achieved in only 1–2 hours for continuous processes. However, it is limited to treating only aqueous wastes due to the ease of surface contact between reducing agent and hazardous constituent. Treatment of slurries, tars and sludges is more difficult due to reduced surface contact. Another limitation of the reduction process is the interference en-

Table VI. Hazardous wastes treated by chromate reduction.

	Waste code	Description
Soluble	U032	Calcium chromate
	D007	Chromium (hexavalent with chromic acid)
	F019	Sludges from chemical conversion coatings
Insoluble	K002	Production sludges from: chrome yellow
	K003	molybdate orange
	K004	zinc yellow
	K005	chrome green oxide
	K006	chrome green oxide
	K008	Oven residues from chrome green oxide
	K086	Pigments and inks
	F006	Insoluble chromates

Table VII. Summary of treatment levels reported for hexavalent chromium wastes.

Treatment process	Chromium (VI) concentration (mg/L) Initial	Final
Reduction		
Sulfur dioxide	1300	"zero"
Sulfur dioxide	0.23–1.5	0.1
Bisulfite	140	0.7–1.0
Bisulfite plus hydrazine	8–20.5	0.1
Metabisulfite	70	0.5
Ion exchange	8–10.7	0.0–0.9
Cementation	16.3	0.09
Activated carbon[a]	0.09–0.19	0.017 (ave.)
Activated carbon[a]	5.0	0.006–0.087
Activated carbon[a]	100–820	5.05–195
Freeze concentration[a]	100	0.225

[a] Pilot plant results.

countered with organic compounds and complexes, causing a decrease in reduction efficiency with a potential for H_2S emission. Furthermore, a large volume of metal hydroxide sludge can be generated.[6]

A two-stage chromate reduction process has been employed for treating chromium plating rinsewater at several waste treatment facilities. In the first stage either sulfur dioxide, sodium bisulfite or metabisulfite are added as reducing agents. In the second "polishing" stage, hydrazine combined with soda-ash is added to precipitate chromic hydroxide. Chromate concentration in the influent ranging from 8 to 20.5 mg/L, was reduced to less than 0.1 mg/L in the effluent.[13]

One study claimed to have successfully reduced chromate by combining two hazardous wastes, chromate and waste pickle liquor, to reduce chromate in the presence of ferrous sulfate. This chemical agent has the purported advantage of being effective, independent of pH.[14]

Several recovery processes have been utilized to recover chromium as a reusable resource. Ion exchange, electrochemical reduction, evaporative recovery, activated carbon and reverse osmosis have all been reported to have some application for hexavalent chromium treatment. Table VII summarizes treatment levels based upon pilot plant results for treating hexavalent chromium wastes.[13]

(2) *Other Reduction Processes.* Reduction of selenites, selenates and osmium tetroxide typically involves reaction with sulfur dioxide. It is reported that selenium precipitates can be recovered. This process was used to remove selenium from copper smelter process wastes. However, this process was only used to recover elemental selenium and was not used for waste treatment. Few established processes have been reported for treatment of osmium tetroxide wastes (RCRA P087). Since osmium tetroxide is an oxidizing agent it has the potential to be reduced by reducing agents such as sulfites.[2]

Stabilization/Solidification

The basis upon which stabilization/solidification (S/S) processes are used is to limit the mobility of pollutants to the groundwater, making land disposal a viable treatment option. Materials are mixed with wastes to chemically and physically immobilize wastes. S/S processes have two different goals. Stabilization functions to reduce the solubility and/or chemical reactivity of a waste, while solidification processes convert the waste into a fixed, easily transported solid with reduced hazard from leaching into the environment.[15]

The process is generally used to treat concentrated waste solids, sludges, slurries and liquid wastewaters.

Malone *et al.*, of USAE Waterways Experiment Station have conducted many studies concerning the application of and factors affecting S/S technology. One study was explicitly devoted to electroplating wastes (RCRA F006-F009).[16] Since the chemical characteristics of electroplating sludges are highly variable, some exhibit varying mixtures of fine grained metal hydroxides, organic chelating agents and salts from materials added for neutralization purposes. These amorphous metal hydroxides of cadmium, chromium, copper, lead, nickel and zinc can become significant pollutants if improper disposal techniques are utilized.

There are two types of S/S agents employed: organic and inorganic additives. Some organic agents presently used are chemical grouts, (e.g. cement) thermoplastic agents (e.g. bitumen, asphalt, paraffin and high temperature polyethylene), organic polymers (e.g. urea-formaldehyde, polyester resins and polyvinyl chloride) and glassification agents (e.g. molten glass). Common inorganic materials used for S/S processes include cement, lime and pozzolan-based agents combined with a mixe[illegible] kiln dust, soluble silicates, fly ash, blast furnace slag and flue gas sludge. Organic processes are expensive and have limited applications, while inorganic processes tend to be less expensive with wider application. However, the inorganic S/S processes are limited by the organic content of the waste.[6]

Some S/S applications lead to the development of chemically stable insoluble silicates which are specific for

Table VIII. Concentrations of cyanide in plating wastewaters.

Process	Range (mg/L)
Plating rinse	1.4–256 (56 avg)
Bright dip	15–20
General (separate cyanide)	9–115 (72 avg)
General (combined stream)	1–103 (28 avg)
Alkaline cleaning bath	4,000–8,000
Plating bath	45,000–100,000
Plating bath	
Brass	16,000–48,000
Bronze	40,000–50,000
Cadmium	20,000–67,000
Copper	15,000–52,000
Silver	12,000–60,000
Tin-zinc	40,000–50,000
Zinc	4,000–64,000

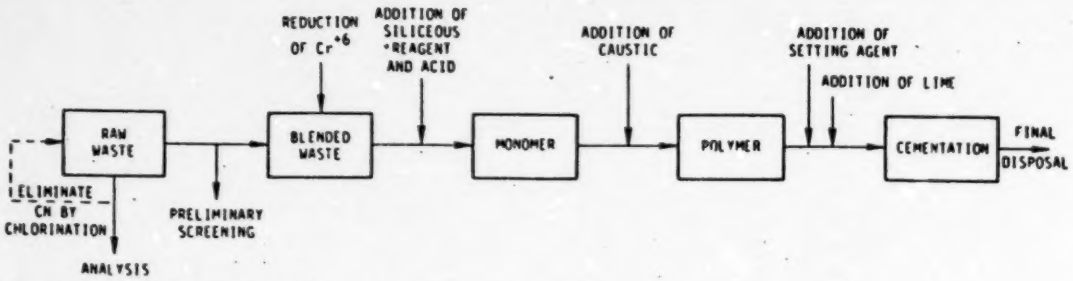


Figure 3. Soliroc process flow diagram.

the metal of interest. Gel-like systems of low-temperature silicate polymers encapsulate the metals in both crystalline and non-crystalline polymeric matrices. Typical encapsulates of metal hydroxides are:

1. Macroencapsulates produced from polymer-bonded and polyethylene jacketed wastes which exhibit excellent containment properties;
2. Microencapsulates produced from organic polymers that are not suitable for electroplating wastes under acidification procedures;
3. Thermoplastic microencapsulates which have shown excellent containment characteristics; and
4. Portland-pozzolan and pozzolan encapsulates exhibiting poor containment properties.

Several studies have shown promising results in stabilizing and solidifying electroplating wastes. One engineering study conducted by Rousseaux and Craig evaluated the "soliroc fixation process" for immobilizing industrial metal wastes.[17] Results indicated that the soliroc process substantially immobilized the metal constituents of sulfuric acid pickle liquor (RCRA K062). Furthermore, the addition of Portland cement in the cementation step improved the structural stability of the hardened material. Figure 3 represents a flow diagram of the process. Compressive strength conducted in this study indicated that the addition of Portland cement in the cementation step improved the stability of the solidified waste.[17]

The U.S. Army Engineer Waterways Experiment Station funded by the EPA has conducted extensive studies on fixation and encapsulation techniques for a variety of industrial wastes including electroplating wastes. Some of the significant findings resulting from these studies have shown that:

1. Lime-fly ash pozzolanic solidification produced a solid soil/cement-like product with good structural integrity but exhibited significant leaching problems;
2. Cement/soluble-silicate techniques produced a semifriable material with soil-like consistency containing 60–70 percent of the metal constituent prevalent in the untreated sludge;
3. Urea-formaldehyde polymerization monomers applied to electroplating waste and paint production sludges failed to contain leaching of the toxic metal constituents; and
4. Encapsulation systems (especially macro-) proved to be the most effective in containing toxic pollutants from electroplating wastes.

Apparent disadvantages encountered with encapsulation techniques are that they tend to be costly and limited to certain waste categories. It is important to note that S/S processes are generally applied to wastewater sludges which cannot be further treated by another means prior to disposal.[18,19]

Cyanide Destruction

One of the major sources of generated cyanide waste is the electroplating industry. Cyanide baths are used to hold metallic ions such as zinc and cadmium in solution. When the "drag-out" of plating solution containing cyanide ions contaminates rinsing baths, a wastewater is generated for treatment. Table VIII lists concentrations of cyanide for representative plating wastewaters.[13]

Cyanide appears in waste residuals in two forms: as an "ionizable cyanide" in the form of sodium cyanide (NaCN) and hydrocyanic acid (HCN) or as a complex with heavy metals, e.g. ferrocyanide, nickel cyanide or copper cyanide. Other cyanide species come in the form of inorganic compounds such as thiocyanates and cyanates which are easily removed from waste streams by using an assortment of treatment processes. Various methods for treating cyanide wastes have been employed, with cyanide destruction via alkaline chlorination being used most frequently. Unit processes reported to successfully treat cyanide and cyanide complexes include incineration, alkaline hydrolysis of cyanohalides, pyrolysis of copper cyanide, peroxide oxidation (Kastone®) and iron cyanide pyrolysis.[2] Although natural degradation including volatilization, oxidation biodegradation and photo decomposition will reduce cyanide concentrations in aqueous wastes given enough time, a recent study has reported successes with ozonation, ion-exchange, activated carbon, reverse osmosis, electrodialysis, electrolytic hydrolysis and titanium oxide/UV.[20]

(*1*) *Alkaline Chlorination.* As the most prominent, widely used treatment option employed to date, alkaline chlorination may be accomplished by direct addition of sodium hypochlorite or by addition of chlorine gas with sodium hydroxide. This process cannot effectively treat simple or complex copper cyanides, zinc cyanide and iron cyanides due to their low solubilities. Hypochlorite, perhaps the most widely used oxidizing agent, reacts with cyanide in the following manner:

$$CN^- H_2O + OCL^- \rightarrow CL - CN + 2OH^- \quad (2)$$

Conversion of CN^- to dissolved cyanogen chloride

$$CL - CN + 2OH^- \rightarrow OCN^- + CL^- + H_2O \quad (3)$$

Hydrolysis of cyanogen chloride

$$2OCN^- + 3OCL^- \rightarrow 2CO_2 + N_2 + 3CL^- + OH^- \quad (4)$$

Conversion to CO_2 and chlorine

If thiocyanates are present the demand for chlorine is preferential, therefore, requiring more oxidant.

The following cyanide bearing

Table IX. Treatment levels for cyanide wastewaters.

Treatment process	Cyanide concentration (mg/L) Initial	Final	Percent removal
Alkaline chlorination[a]		1.7	
Alkaline chlorination[a]		0.1	
Alkaline chlorination[b]		0.4	
Alkaline chlorination[b]	700	0.0	100
Alkaline chlorination	32.5	0.0	100
Alkaline chlorination[c]	5.1	0.1	98
Ferro-ferrocyanide precipitation		5–10	
Electrolysis	45,000–100,000	0.1–0.5	99.99+
Electrolysis	20	0.5	97.5
Ozonation	25	0	100
Kastone process	350–400	0.3	99.9+

[a] Single-stage chlorination.
[b] Two-stage chlorination.
[c] High pH-high temperature process.

wastes are amenable to alkaline chlorination:

RCRA Waste Code	*Waste*
P106	Sodium cyanide
P098	Potassium cyanide
P021	Calcium cyanide
P013	Barium cyanide (the treated waste requires subsequent treatment by the sulfate precipitation process)
P083	Hydrogen cyanide (in aqueous solution)
P074	Nickel cyanide
P099	Potassium silver cyanide (sludges generated may be reprocessed to recover silver)
P104	Silver cyanide (sludges generated are reprocessed for silver recovery)
K060	Lime sludge from coking operations
F006–12	Cyanide bearing plating solutions and sludges (some treated sludges may be reprocessed to recovery metals; sludges of no value may require subsequent treatment by the encapsulation process)
P030	Miscellaneous cyanides

(2) *Incineration.* Incineration has been used to destroy gaseous hydrogen cyanide, gaseous cyanogen, organonitriles and organic isocyanates at elevated temperatures. Several types of incinerators such as liquid injection, rotary kiln and fluidized bed are capable of treating these wastes. Isocyanates are converted to CO_2, N_2, and H_2O leaving little if any toxic residuals. The following cyanide wastes may be treated by incineration.[2]

RCRA Waste Code	*Waste*
P083	Hydrogen cyanide (as gas)
U003	Acetonitrile
U152	Methyl acrylonitrile
U149	Propane nitrile
U009	Acrylonitrile
P101	Propionitrile
P064	Methyl isocyanate
P069	2-Methylacetonitrile
P027	3-Chloropropanenitrile
P069	2-Hydroxy-2-methylpropanenitrile
P031	Cyanogen
K011–14	Waste streams for acrylonitrile and acetonitrile production
K087	Tar sludges from coking operations
U223	Toluene diisocyanate

(3) *Other Cyanide Processes.* Since iron cyanides, such as ferric cyanide (RCRA P055), chrome green (RCRA K005), iron blue (RCRA K007) and paint/ink formulation sludges (RCRA K086) are not easily treated by chlorination processes due to the stability of the iron ion, decomposition of the complex to yield free cyanide ions is a prerequisite. Ultraviolet (UV) radiation has been reported to be effective in converting complex cyanides to cyanate.[20]

Ozonation has been demonstrated to show potential for treating relatively dilute cyanide wastes, e.g., rinse water plating wastes or "carryover" from electrolytic decomposition.[13] The free cyanide reaction with ozone can be represented as:

$$CN^- + O_3 \rightarrow CNO^- + O_2 \quad (5)$$

with the reaction proceeding rapidly. Conversion of cyanate to bicarbonate and nitrogen is slower:

$$2CNO^- + 3O_3 + H_2O \rightarrow 2HCO_3^- + N_2 + 3O_2 \quad (6)$$

Thiocyanate reacts rapidly with ozone, hence requiring a much greater demand for ozone to complete the reaction. Ultraviolet light can be used in conjunction with ozone to treat wastes generated from electroplating and color photographic processes. One of the disadvantages of using ozone and/or ozone/UV treatment is the high energy consumption.[20]

The Kastone® process purportedly removes free cyanide from wastewaters generated by an electroplating industry. Free cyanide is converted to a mixture of ammonia, sodium cyanate and

Table X. Summary of observed metals removals.

Metal	Influent (mg/L)	Primary effluent (mg/L)	Removal by pri. clar. (percent)	Activated sludge effluent (mg/L)	Removal by activated sludge (percent)	Total removal (percent)
Ag	8.0	9.0	0.0	5.0	44.0	37.5
As[a]	20.6	16.0	22.3	16.7	0.0	18.9
Ca	86.0	81.0	5.8	81.0	0.0	5.8
Cd[a]	20.9	17.0	18.7	7.9	53.5	62.2
Cr	0.63	0.51	19.0	0.34	33.3	46.0
Cu	0.80	0.57	28.8	0.16	71.9	80.0
Fe	4.29	2.44	43.1	1.01	58.6	76.5
Hg[a]	2.0	2.0	0.0	2.0	0.0	0.0
Mg	17.6	28.0	0.0	17.9	0.0	0.0
Mn	0.65	0.55	15.4	0.40	27.3	38.5
Ni	0.45	0.27	40.0	0.18	33.3	60.0
Pb	0.88	0.58	34.1	0.11	81.0	87.5
Zn	1.24	1.28	0.0	0.46	64.1	62.9

[a] Micrograms/liter.

Table XI. Influence of heavy metals on cyanide biodegradation.[a]

Metal (no. of observations)		Metal conc. (mg/L) Influent	Metal conc. (mg/L) Effluent mean (S.D.)	Cyanide as CN, mg/l Influent mean (S.D.)	Cyanide as CN, mg/l Effluent mean (S.D.)
Zinc	(8)	10	0.07 (N.C.)	98.6 (6.63)	0.20 (0.01)
	(8)	25	0.04 (N.C.)	97.4 (2.67)	0.18 (0.01)
	(8)	50	0.12 (0.19)	98.2 (6.96)	0.19 (0.02)
Cadmium	(9)	5	0.13 (0.02)	95.6 (3.50)	0.17 (0.02)
	(5)	10	0.60 (0.50)	97.4 (7.00)	0.18 (0.02)
	(5)	20	0.56 (0.09)	100.0 (0.76)	0.18 (0.01)
Copper	(7)	5	4.06 (1.28)	96.7 (2.45)	2.00 (0.40)
	(6)	10	8.50 (0.56)	96.1 (2.00)	16.20 (3.60)
	(6)	20	17.60 (1.00)	97.0 (1.00)	28.50 (2.00)

[a] S.D.—standard deviation; N.C.—not calculated.

glycolic acid amide in the presence of formaldehyde and a proprietary formulation containing hydrogen, peroxide, stabilizers and flocculants. Although free cyanides are destroyed, a resultant increase in BOD/COD and sediments would require further wastewater treatment. Another disadvantage of the process is the use of formaldehyde, a suspected carcinogen.[21]

Although ion exchange, activated carbon, reverse osmosis and electrodialysis have been mentioned as feasible treatment options for treating cyanide wastes, these processes are directed at removal, not destruction of the cyanide. These processes will be covered in another section addressing reduction and recovery techniques. A summary of treatment levels for typical wastewaters is presented in Table IX.[13]

Biological Treatment

Although biological treatment of wastes containing metal constituents has traditionally been reserved for POTWs treating municipal wastes containing low concentrations of metal ions, recent studies have attempted to treat higher strength aqueous metal wastes, such as cyanide, mercury, and arsenic. Microbes may be utilized to convert more toxic forms of heavy metals into less toxic forms (e.g., $Hg^{2+} \rightarrow Hg^{\circ}$).[22,23]

In a study conducted by Petrasek, at EPA's Test and Evaluation Facility, Cincinnati, Ohio, an activated sludge system was monitored for low concentration metals removal. Metals removals were computed and material balances established for 13 prevalent metal ions in a municipal wastewater. Results are presented in Table X.[24] The average removal of the 13 metals, based upon mass balance calculations was 42 percent. The best removal efficiency of all 13 metal ions monitored was exhibited by Pb with 87.5 percent removal.

Data on the biological treatment of higher strength metal wastes are more limited. It has been documented by Silver and Misra[22] that certain bacteria can carry out chemical transformations of heavy metals. Transformations can occur via intra- and extracellular metabolism of the various elements. These transformations include oxidation, reduction, methylation and dimethylation of certain metal ions. However, these transformations are sometimes byproducts of normal metabolism with. These transformations can constitute a mechanism for resistance which are often determined by plasmids.

The mercury cycle represents the best known example of how microbes metabolize the chemical form of a metal ion; as is represented below:

$$CH_3Hg^+ \rightleftharpoons Hg^{2+} \rightleftharpoons Hg^{\circ} \quad (7)$$

The enzymatic mechanism responsible for mercurial detoxification volatilizes the mercury as metallic Hg° by an enzyme called mercuric reductase (R100). Although work has been done on other select material (e.g. silver, cadmium, and zinc) little is known for other toxic metals. However, there is some preliminary evidence that certain microbes can be fooled into accumulating toxic metals.[22]

Another study on the biological treatment of an industrial wastewater containing toxic cyanide was conducted by Shivaraman and Parhad.[25] Although aklaline chlorination is the preferred method for cyanide destruction, biological treatment systems have shown some cost advantages in treating cyanide and cyanide-complexed wastewaters. It has been demonstrated that "simple" cyanide can be degraded by activated sludge systems and trickling filters when these systems have been acclimated prior to full loading. Moreover, zinc and cadmium cyanide complexes were shown to be degraded via acclimated trickling filters. Results are shown in Table XI. As evidenced, good removal efficiencies were observed for Zn, Cd and their respective cyanide complexes; however, Cu exhibited poor treatability.

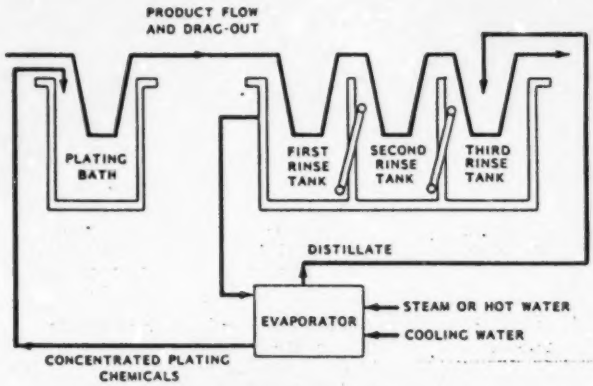
Waste Reduction and Recovery

Interest in establishing centralized treatment and recovery systems for treating heavy metal wastes in large metropolitan areas has spurred many studies to demonstrate waste reduction and recovery technologies. With the high cost of raw materials and pending land disposal restrictions (HSWA), reclamation of raw materials from waste streams can be the treatment option of choice. EPA studies indicate that a large part of the operational costs would be subsidized by the sale of the recovered metals.[26] An estimate of metal values lost in 1980 is presented in Table XII. Using the same amount of metals discarded and adjusting for inflation, the 1985 estimate would increase to $58 million.[27]

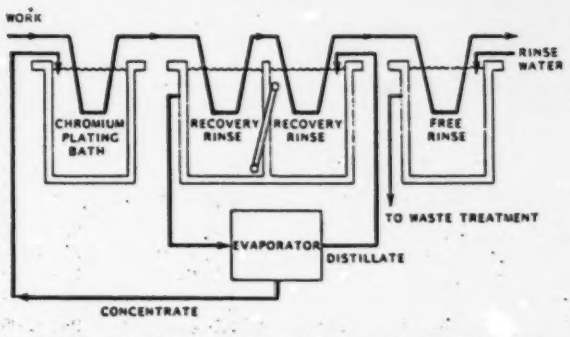
Economic feasibility of metals recovery operations are primarily dependent upon three factors:

Table XII. Annual loss of minerals in electroplating wastes.

Mineral	Amount (metric tons)	Value/ton	Total value
Iron	3,460	$ 77	$ 266,420
Copper	2,560	791	2,024,960
Zinc	3,718	748	2,781,064
Nickel	5,000	4,000	20,000,000
Aluminum	1,651	1,060	1,750,060
Chromium	6,357	2,000	12,714,000
Lead	756	462	349,272
Total	23,502		$39,885,776



1—Closed-Loop Evaporative Recovery System.



2—Open-Loop Evaporative Recovery of Chromium Plating Drag-Out.

Figure 4. Evaporative recovery systems.

1. Metal type and concentration;
2. Availability of material quantity within close proximity; and
3. Economical (profitable) recovery process.

Justification for recovery processes is not exclusive to raw material savings. Reduced operating costs for "end-of-pipe" pollution control can be a significant factor. Four reduction and recovery processes will be discussed here: evaporation processes, ion-exchange systems, membrane technology, and electrolytic deposition.

Evaporation

Evaporators have traditionally been used to concentrate rinse water and recycle "drag-out" back to the plating bath. This in-plant separation process represents a sound waste minimization practice. Figure 4 illustrates two types of systems which have been employed: 1) a closed-loop system, which totally eliminates a water discharge from the plating process and requires substantial make-up water to satisfy rinsing requirements and 2) an open-loop system with lower operating costs as a result of less make-up water. However, with the open-loop system a wastewater discharge is generated.

Ion Exchange

Ion exchange (I/E) and resin adsorption systems offer a versatile separation process with wide application to the metal finishing industry. I/E has all the advantages of evaporative processes for recovery. In addition, it can serve as a polishing step after conventional wastewater treatment and purification of liquids (acids, bases, water, etc.). By definition, I/E is a separation technology which removes various ionic species from solution via interchanging reversible ions between the solution (aqueous waste) and the exchanger (e.g. resin). The I/E process can be manifested as a resin system, membrane selection process (Donnan Dialysis) or a liquid-liquid extraction procedure. Exchangers may be comprised of synthetic resins, insoluble salts, molecular sieves or even liquid membranes. Liquid ion exchange, where organic polar molecules are added to complexed metal ions, appears to have some promise.[28]

Many applications for ion-exchange systems have been demonstrated. The development of reciprocating flow and countercurrent exchange systems have enhanced the potential application of I/E for plating "drag-out" recovery by 1) providing reduced equipment cost (due to small resin volumes), 2) automatic regeneration of resin, and 3) their compact size. These systems are currently being used for drag-out recovery from chromium, copper and nickel plating rinses, purification of spent process acids (e.g. chromic acid) and mixed wastewater deionization. Figure 5 shows a schematic of an I/E system utilized for polishing following conventional treatment.

Several studies have been conducted to demonstrate specific application of various resins for treating synthetic and industrial aqueous metal wastewaters. Tare *et al.*[29] described the kinetics for metal ion removal by chelating I/E resins. The presence of strongly complexing organics (such as citrate, EDTA, and tartrate) and inorganic ligands (CL, F, PO_4, etc.) in dilute metals waste make chemical separation processes (i.e. precipitation) not feasible. Chelating I/E resins offer an alternative to treating these complexed wastes. Results of this study have shown that rates of metal uptake were strongly influenced by solution pH and waste aging, especially for Cr (III) and Pb. Desorption from contacted resins was easily achieved by using hydrochloric acid.

In another study, Maeda[30] investigated the influence of porosity for several macroreticular chelating resins (RST) containing triethylene-tetramine with different porosities. Results indicated that large pore radius RSTs proved to be more practical for removal and recovery of heavy metal ions from an industrial metal bearing waste.

Liquid ion exchange is a relatively new process which combines the concepts of I/E and liquid-liquid extraction for the recovery of metal ions from wastes.[31] This application has shown promise for treating the more dilute metal wastewaters. Like resin systems, the actual exchange takes place when the solution of metal ions, upon contact with the extractant, produces an unstable liquid-liquid dispersion. The process occurs via a three-step mechanism:

1. The complexed metal ion diffuses to the aqueous/organic interface;
2. The ion is stripped of its hydration layer and complexes with the extractant at the interface; and
3. The organic/metal complex diffuses into the bulk organic phase where, simultaneously, hydrogen ions are transferred to the aqueous phase.

Thereafter, the stripping solution (extractant) is regenerated.

Additional research is needed to further develop I/E processes. Potential areas include: the development of bet-

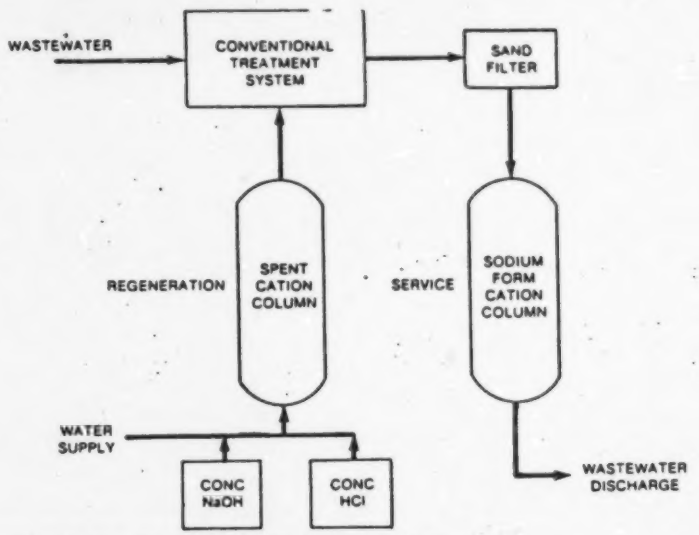


Figure 5. Ion exchange polishing after conventional treatment.

ter ion-exchange materials which do not foul as easily, investigation of the transport of ionic species through a dielectric medium, improvement of counter current processes, and further development of liquid I/E systems.

Membrane Processes

Membrane processes typically used to treat aqueous metal wastes are reverse osmosis (RO) and electrodialysis. RO is a pressure driven membrane process where water molecules are forced through the microscopic pores of a semi-permeable membrane.The production rate of an RO membrane is a function of dissolved solids concentration, temperature, pressure, pH and chemistry of the solution to be treated. No commercially available membrane polymer has demonstrated tolerance to all extreme chemical factors, such as pH, strong oxidizing agents, and aromatic hydrocarbons.

A study by Crampton[26] successfully demonstrated the use of a cellulose acetate membrane to concentrate the drag-out from plating solutions. Both the concentrate and purified water are recycled. However, this type of membrane is pH sensitive and is primarily used to treat Watt's nickel plating baths. Other drag-out recovery applications successfully treated copper, zinc and chromic acid baths.

Cartwright defines various membrane types and their applications.[32] Some applications of RO membranes to various waste streams are listed below:

Nickel—cellulose acetate

Copper sulfate—hollow-film polyamide, cellulose triacetate and spiral-wound-thin film composite

Zinc sulfate—spiral-wound-thin film composite

Brass cyanide—polyamide cellulose, triacetate hollow fiber

Copper cyanide—polyamide hollow fiber

Chromium (VI)—spiral-wound-thin film composite

Other—thin film composite (TFC)

Table XIII presents RO test data for six common plating bath rinses.[32]

Potential problems with RO systems stem from membrane fouling due to suspended precipitated solids coating the membrane surface, precipitation of salts in the concentrate, membrane deterioration due to chemical attack and, for higher strength wastes, high levels of dissolved solids in the permeate.

In electrodialysis systems an electrical potential is applied across the membranes to provide the driving force for ion passage through the membranes. Membranes used in this process are "thin sheets" of the same polymeric network used to make I/E resins. Unlike RO systems, these membranes are tolerant of most chemical environments. Another variance exhibited by electrodialysis over RO systems is the propensity to separate water from the salt by selective removal of the salt, rather than concentrating the salt from solution.

Electrolytic Recovery

Electrolytic recovery is one of the many technologies utilized to remove and concentrate metals from process waste streams. This process uses electricity to pass a current through an aqueous metal bearing solution between a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit which is strippable and recoverable. Initially used to recover gold and silver, its use in recovering less precious metals has been limited. However, new interest has been given to this promising recovery technology.

Walters and Vilagliana of the University of Maryland have demonstrated the electrolytic recovery of zinc from metal finishing rinse waters.[33] The deposition of copper ions after contacting diluted aqueous metals solution onto a packed graphite bed was studied. Results of the study indicated that zinc recovery from plating bath rinse waters, which consisted of a dilute zinc cyanide solution, was achievable. A batch electrochemical reactor with stainless steel electrodes was employed. The controlling factor in achieving high rates of zinc deposition appeared to be agitation. The study

Table XIII. RO test data for six common plating bath rinses.

Plating bath	Bath temperature °C/°F	Toxic contaminant	Percent rejection
Watts Ni	60/140	Ni^{2+}	99+
Copper cyanide	60/140	Cu^{+}	85
		CN^{-}	46
Zinc cyanide	27/80	ZN^{2+}	96
		CN^{-}	80
Brass cyanide	27/80	ZN^{2+}	98
		Cu^{+}	97
		CN^{-}	
Decorative Cr	43/110	Cr^{6+}	90
Hard Cr	55/130	Cr^{6+}	92

cited that mechanical mixing and nitrogen gas aeration were both effective. NaCl was added to maintain a minimal conductivity level. Higher current densities elicited higher deposition rates as opposed to lower current densities. One noticeable disadvantage was that corrosion could play a significant limiting factor. Electrodes would have to be replaced frequently.

Summary

A review of applicable technologies for any given time tends to be a mere "snapshot" of the advances and development of treatment options that enable industry to keep pace with economic realities and legislative requirements. Although this review only scratches the surface of available technologies for metals treatment application, numerous innovative approaches deserve evaluation. Many options have been presented with specific application to hazardous waste treatment of metal bearing process residuals. With proper application, most processes discussed here can lead to responsible hazardous waste management.

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